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Low-temperature Molten Sodium Batteries for Large-Scale Storage: Fundamental Studies of Metal Halide Catholyte and Cathode Materials

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Low-cost, long-duration energy storage is a vital resource needed for a robust electric grid powered by renewables. Low-temperature (<130 °C) molten sodium batteries (MNaBs) with NaI-metal halide molten salt catholytes have been developed to meet this need. This battery chemistry avoids the safety concerns caused by metal dendrites and flammable organic solvents found in Li-metal or Li-ion batteries. It also offers higher voltages and drastically reduces the expensive high temperature material requirements compared to other MNaBs, such as sodium-nickel chloride (ZEBRA) batteries, which operate near 300 °C. Among the key challenges to wide-spread utilization of these emerging molten Na batteries for large-scale, long-duration applications is catholyte stability and performance at high current densities while cycling at temperatures just above the melting point of Na (98 °C). To optimize the catholyte, we have examined a variety of electroactive molten salt chemistries, including mixtures of NaI with $AlCl_3$, $AlBr_3$, and $GaCl_3$. To better understand the catholyte properties during cycling, we have performed electrochemical kinetics studies and mathematical modeling of the iodide-triiodide speciation. Results reveal a dependence between catholyte speciation and usable capacity and current densities for the given catholyte compositions. Additional experiments, including cyclic voltammetry and chronoamperometry, probe the interactions between the cathode current collector and the molten salts, revealing potential impacts on electrochemical kinetics and

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stability during cycling. Insights from these fundamental studies serve as the foundation for the informed design of high-performance cathodes in new scalable molten sodium batteries.

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